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[Document Type] Specification

[Title of the Invention] PRINTING PLATE MATERIAL AND METHOD FOR RENEWAL THEREOF

[Claims]

[Claim 1] A printing plate material comprising a substrate on the surface of which a coat layer containing a titanium oxide photocatalyst and one or two or more of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+} is formed directly or with an intermediate layer intervening.

[Claim 2] The printing plate material as recited in claim 1, wherein the surface of said coat layer has hydrophobicity in terms of a water contact angle of at least 50° or greater in its initial state during preparation of a printing plate and is converted into a hydrophilic surface having a water contact angle of 10° or less by irradiation of the surface with light having a wavelength at an energy level higher than a band gap energy level of the titanium oxide photocatalyst.

[Claim 3] The printing plate material as recited in claim 1, wherein the surface of said coat layer, which has hydrophobicity in terms of a water contact angle of at least 50° or greater in its initial state during preparation of a printing plate, is converted into a hydrophilic surface having a water contact angle of 10° or less by irradiation with the light having a wavelength at an energy level higher than a band gap energy level of the titanium oxide photocatalyst and the hydrophilic surface serves as a non-printing image portion and the remaining hydrophobic surface serves as a printing image portion.

[Claim 4] The printing plate material as recited in any of claims 1 to 3, wherein the surface of said coat layer being hydrophilic in at least one portion of the surface thereof is reconverted into a hydrophobic surface having a water contact angle of at least 50° or greater by the irradiation of an energy flux thereon.

[Claim 5] The printing plate material as recited in any of claims 1 to 3, wherein the surface of said coat layer being hydrophilic in at least one portion of the surface thereof is reconverted into a hydrophobic surface having a water contact angle of at least 50° or greater by carrying out a chemical treatment thereon.

[Claim 6] The printing plate material as recited in any of claims 1 to 3, wherein the surface of said coat layer being hydrophilic in at least one portion of the surface thereof is reconverted into a hydrophobic surface having a water contact angle of at least 50° or

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[Title of the Invention] PRINTING PLATE MATERIAL AND METHOD FOR RENEWAL THEREOF

[Claims]

[Claim 1] A printing plate material comprising a substrate on the surface of which a coat layer containing a titanium oxide photocatalyst and one or two or more of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and $Cu^{2+}$is formed directly or with an intermediate layer intervening.

[Claim 2] The printing plate material as recited in claim 1, wherein the surface of said coat layer has hydrophobicity in terms of a water contact angle of at least 50° or greater in its initial state during preparation of a printing plate and is converted into a hydrophilic surface having a water contact angle of 10° or less by irradiation of the surface with light having a wavelength at an energy level higher than a band gap energy level of the titanium oxide photocatalyst.

[Claim 3] The printing plate material as recited in claim 1, wherein the surface of said coat layer, which has hydrophobicity in terms of a water contact angle of at least 50° or greater in its initial state during preparation of a printing plate, is converted into a hydrophilic surface having a water contact angle of 10° or less by irradiation with the light having a wavelength at an energy level higher than a band gap energy level of the titanium oxide photocatalyst and the hydrophilic surface serves as a non-printing image portion and the remaining hydrophobic surface serves as a printing image portion.

[Claim 4] The printing plate material as recited in any of claims 1 to 3, wherein the surface of said coat layer being hydrophilic in at least one portion of the surface thereof is reconverted into a hydrophobic surface having a water contact angle of at least 50° or greater by the irradiation of an energy flux thereon.

[Claim 5] The printing plate material as recited in any of claims 1 to 3, wherein the surface of said coat layer being hydrophilic in at least one portion of the surface thereof is reconverted into a hydrophobic surface having a water contact angle of at least 50° or greater by carrying out a chemical treatment thereon.

[Claim 6] The printing plate material as recited in any of claims 1 to 3, wherein the surface of said coat layer being hydrophilic in at least one portion of the surface thereof is reconverted into a hydrophobic surface having a water contact angle of at least 50° or

greater by a combination of chemical treatment and irradiation of energy.

[Claim 7] The printing plate material as recited in any of claims 1 to 3, wherein the surface of said coat layer being hydrophilic in at least one portion of the surface thereof is reconverted into a hydrophobic surface having a water contact angle of at least 50° or greater by an abrasive cleaning of the surface and a renewing of the coat layer containing the titanium oxide catalyst.

[Claim 8] A printing plate material comprising a substrate, the surface of which comprises a coat layer containing a titanium oxide photocatalyst and at least one or two or more of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+} formed directly or with an intermediate layer intervening, and a coating layer comprising a chemical compound which can be decomposed by irradiation with light having a wavelength at an energy level higher than a band gap energy level of the titanium oxide photocatalyst on the coat layer.

[Claim 9] The printing plate material as recited in claim 8, wherein the coating layer surface has hydrophobicity in terms of a water contact angle of at least 50° or greater in its initial state during preparation of a printing plate, and, along with causing said coat layer surface to emerge, the coat layer surface is converted into a hydrophilic surface having a water contact angle of 10° or less by irradiation of said light onto said coating layer surface.

[Claim 10] The printing plate material as recited in claim 8 wherein, by the irradiation of light onto a surface of said coating layer which has hydrophobicity in terms of a water contact angle of at least 50° or greater in its initial state during preparation of a printing plate, in a region irradiated with the light, a surface of said coat layer is caused to emerge and the surface of the coat layer is converted into a hydrophilic surface having a water contact angle of 10° or less, wherein the surface which becomes hydrophilic serves as a non-printing image portion and the remaining hydrophobic surface serves as a printing image portion.

[Claim 11] The printing plate material as disclosed in claims 1 to 10, wherein said one or two or more of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+} is contained as an oxide.

[Claim 12] The printing plate material as recited in any of claims 1 to 10, wherein said one or two or more of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+} is contained as an oxide compound with titanium.

[Claim 13] A method for renewing a printing plate material comprising a substrate on the surface of which a coat layer containing a titanium oxide photocatalyst and one or two or more of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+} is formed directly or with an intermediate layer intervening, the method comprising at least the steps of:

cleaning a surface of a coat layer containing a titanium oxide photocatalyst after completion of printing; and then

renewing the coat layer containing a titanium oxide photocatalyst.

[Claim 14] A method for renewing a printing plate material in which the surface of the coat layer being reconverted to become a hydrophobic surface as recited in any of claims 4 to 7, wherein a step of reconverting the coat layer is performed in a printing machine.

[Claim 15] A method for renewing a printing plate material comprising a substrate, the surface of which comprises a coat layer containing a titanium oxide photocatalyst and at least one or two or more of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+}formed directly or with an intermediate layer intervening, and a coating layer comprising a compound which can be decomposed by irradiation with light having a wavelength at an energy level higher than a band gap energy level of the titanium oxide photocatalyst on the coat layer, the method comprising at least the steps of:

cleaning an outermost surface including a surface of the coat layer which is hydrophilic in at least one portion thereof after completion of printing; then

reforming the coating layer to cause a hydrophobic surface having a water contact angle of 50° or more to emerge; and then

irradiating the light onto the coating layer surface.

[Claim 16] A method for renewing a printing plate material, wherein the method of renewing the printing plate material recited in claim 15 is performed in a printing machine.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to a printing plate material and to a method for renewal thereof.

[0002]

[Prior Art]

In the field of printing technology in general, digitization of printing process has recently been advancing. This technology involves digitalizing via a personal computer or the like of image data which has been read by a scanner or the like, and related to the preparation of a printing plate, trying to use directly the digital data. This allows labor-saving in the whole printing process and facilitates high definition printing.

[0003]

Hitherto, there has been generally used as a plate for use in printing a so-called PS plate which has anodized aluminum as a hydrophilic non-image part and a hydrophobic image part formed by curing a light-sensitive resin on a surface of the non-image part. Printing is carried out by ink adhering to the abovementioned hydrophobic image part being transferred onto paper. Understandably, PS plates have not been compatible with the abovementioned digitization of printing processes.

[0004]

On the other hand, other than the abovementioned PS plates, methods have been proposed to facilitate preparation of printing plates in accordance with the digitization of printing processes. For example, there are known methods which comprise providing a PET film having coated thereon a laser absorbing layer such as a carbon black layer and a silicone resin layer in order and imagewise irradiating the film with laser light to generate heat in the laser absorbing layer to burn off the silicone resin layer by the heat to prepare a printing plate, methods which comprise coating an oleophilic laser absorbing layer on an aluminum plate and a hydrophilic layer on the oleophilic laser absorbing layer, and irradiating the hydrophilic layer with laser light to burn it off to make a printing plate, and the like.

[0005]

[Problems to be Solved by the Invention]

With the abovementioned technology, however, problems such as the following have occurred. First, preparation of the abovementioned PS plates requires much time and money; thus, being a prime factor of printing cost increases, particularly for the printing of a small numbers of copies. Furthermore, labor is required for exchanging printing plates

when the printing of one design ends and printing of the next is undertaken; thus, used printing plates have conventionally been discarded. Still further, as mentioned above, PS plates have not been conformed to the digitalization of printing processes. In other words, with PS plates, direct preparation of printing plates from digital data has not been attained, and the realization of digitalization of printing processes in order to realize power saving and high-definition printing has been impossible.

[0006]

The abovementioned preparation of printing plates which are compatible with digitalization, that is, those which use PET films or use aluminum plates, is certainly possible with respect to the preparation of printing plates directly from digital data; however, when the printing of one design is over, the printing plate must be exchanged by a new one before the next printing can be performed. Therefore, printing plates used once must be disposed of and, in this regard, the above methods are the same as the method which uses the PS plate. That is, the cost of printing increases accordingly. From the viewpoint of protection of the global environment which recently has come to be frequently advocated, the disposal of plates which have been used once is undesirable.

[0007]

The present invention was completed in view of the abovementioned circumstances; thus, an object thereof is providing a printing plate such that it is compatible with the digitalization of printing processes, while allowing reuse of material and providing a method for renewal therefor.

[0008]

[Means for Solving the Problems]

In order to solve the above problems, the present invention has taken the following countermeasures.

That is, the printing plate material according to claim 1 comprises a substrate on the surface of which a coat layer containing a titanium oxide photocatalyst and one or two or more of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and $Cu^{2+}$is formed directly or with an intermediate layer intervening.

[0009]

Upon irradiation of a surface of the coat layer having hydrophobicity with light,

those portions of the printing plate material of the invention irradiated become hydrophilic. This is attributable to the effect of the titanium oxide photocatalyst; however, by incorporating one or two or more of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+}, the phenomenon of hydrophilization is promoted, and faster preparation of a printing plate is made possible. Utilization of the portions which have become hydrophilic as a non-printing image portion to which no ink will adhere and the remaining hydrophobic portion as a printing image portion to which ink will adhere allows the material to exhibit its function as a printing plate material. In the case where an intermediate layer is provided between the substrate and the coat layer, the adhesion strength of the coat layer can be maintained at a sufficient level.

[0010]

The printing plate material as recited in claim 2 is one wherein the surface of the coat layer has hydrophobicity in terms of a water contact angle of at least 50° or greater in its initial state during preparation of a printing plate and is converted into a hydrophilic surface having a water contact angle of 10° or less by irradiation of the surface with light having a wavelength at an energy level higher than a band gap energy level of the titanium oxide photocatalyst.

[0011]

Accordingly, in the initial state when a printing plate is prepared, the entire printing plate surface can attain the state wherein it becomes an image part. Furthermore, the coat layer surface irradiated with light having a wavelength at an energy level higher than a band gap energy level of the titanium oxide photocatalyst can be used as a non-image portion because of conversion into a hydrophilic surface. Moreover, light irradiation, for example, can be made to occur based on digital data that conform with the image to be printed, in which case, the printing plate material according to the present invention becomes one which accommodates digitalization of printing processes.

[0012]

The printing plate material as recited in claim 3, is one wherein the surface of said coat layer, which has hydrophobicity in terms of a water contact angle of at least 50° or greater in its initial state during preparation of a printing plate, is converted into a hydrophilic surface having a water contact angle of 10° or less by irradiation with the light

having a wavelength at an energy level higher than a band gap energy level of the titanium oxide photocatalyst and the hydrophilic surface serves as a non-printing image portion and the remaining hydrophobic surface serves as a printing image portion.

[0013]

Thus, the printing plate material is one which has the same effects as the invention disclosed in the abovementioned claim 2. Accordingly, the printing plate material is one which allows conformity with digitalization of printing processes.

[0014]

The printing plate material as recited in claim 4 is one wherein the surface of the coat layer being hydrophilic in at least one portion of the surface thereof is reconverted into a hydrophobic surface having a water contact angle of at least 50° or greater by the irradiation of an energy flux thereon.

[0015]

Accordingly, since the coat layer surface which includes a hydrophilic part is converted to hydrophobic part by the irradiation of an energy flux, the printing plate material can be regarded as having turned into an initial state. That is, this means that the printing plate material can be used again.

[0016]

The printing plate material as recited in claim 5 is one wherein the surface of the coat layer being hydrophilic in at least one portion of the surface thereof is reconverted into a hydrophobic surface having a water contact angle of at least 50° or greater by carrying out a chemical treatment thereon.

[0017]

By carrying out a chemical treatment as a substitute for the energy flux, the same effect as that of the printing plate material of claim 4 can be attained.

[0018]

The printing plate material as recited in claim 6 is one wherein the surface of the coat layer being hydrophilic in at least one portion of the surface thereof is reconverted into a hydrophobic surface having a water contact angle of at least 50° or greater by a combination of the chemical treatment and the irradiation of energy.

[0019]

By carrying out the energy flux and chemical treatment combined, the same effect as that of the printing plate material of claim 4 can be attained. In this case, to convert the hydrophilic surface into a hydrophobic surface, a plurality of means are used; thus, it is conceivable that the conversions can generally be completed swiftly.

[0020]

The printing plate material as recited in claim 7 is one wherein the surface of the coat layer being hydrophilic in at least one portion of the surface thereof is reconverted into a hydrophobic surface having a water contact angle of at least 50° or greater by an abrasive cleaning of the surface and a renewing of the coat layer containing the titanium oxide catalyst.

[0021]

This is achieve, for example, by the forming of a new coat layer on a hydrophilic surface. Thus, the entire printing surface becomes hydrophobic, that is, initial conditions are made to arise in which the entire surface becomes a non-image part. Accordingly, it becomes possible to elicit the same effects as those which are derived based on claim 4. That is, this means that the printing plate material can be used again.

[0022]

The printing plate material as recited in claim 8 comprises a substrate, the surface of which comprises a coat layer containing a titanium oxide photocatalyst and at least one or two or more of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+} formed directly or with an intermediate layer intervening, and a coating layer comprising a chemical compound which can be decomposed by irradiation with light having a wavelength at an energy level higher than a band gap energy level of the titanium oxide photocatalyst on the coat layer.

[0023]

The surface of the printing plate material can be divided into hydrophobic and hydrophilic regions by the action of titanium photocatalyst oxides and compounds. Furthermore, hydrophilic images are facilitated by the inclusion of one or two or more of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+} within the coat layer, thus allowing faster preparation of plates. Moreover, the hydrophilic region is emerged by irradiating light (in general, ultraviolet light). by using the portion converted to become hydrophilic as the non-image portion to which ink is not adhered and using the remaining hydrophobic portion as an

image portion to which ink is adhered, the manifestation of a function as a printing plate becomes possible. Moreover, when an intermediate layer intervenes between the substrate and the coat layer, the bond strength of the coat layer can be sufficiently secured.

[0024]

The printing plate material as recited in claim 9 comprises the printing plate material as recited in claim 8, wherein the coating layer surface has hydrophobicity in terms of a water contact angle of at least 50° or greater in its initial state during preparation of a printing plate, and, along with causing the coat layer surface to emerge, the coat layer surface is converted into a hydrophilic surface having a water contact angle of 10° or less by irradiation of light onto the coating layer surface.

[0025]

This printing plate material, in the initial state during preparation of a plate, can attain the state in which the entire surface is an image portion. Furthermore, since the coat layer irradiated with light having a wavelength at an energy level higher than a band gap energy level of the titanium oxide photocatalyst is converted into a hydrophilic surface, this portion can be used as a non-image portion. It should be noted that in hydrophilic chemical treatment, the attainment of effects such as those shown below is indicated. Namely, due to the titanium oxide catalyst, that is, due to the inherent "catalyst" effects thereof, there is the effect of promoting decomposition of the compounds and the effect of the titanium oxide catalyst itself becoming a hydrophilic surface having a water contact angle of 10° or more. Accordingly, in this case, the attainment of swift completion of the hydrophilic chemical treatment can be presumed. Moreover, it become possible for the ultraviolet light radiation, for example, to be carried out based on digital data which conforms to an image to be printed. In this case, the printing plate material according to the present invention, has becomes one which accomodates digitalization of printing processes.

[0026]

With the printing plate material as recited in claim 10, by the irradiation of light onto a surface of the coating layer which has hydrophobicity in terms of a water contact angle of at least 50° or greater in its initial state during preparation of a printing plate, in a region irradiated with the light, a surface of the coat layer is caused to emerge and the

surface of the coat layer is converted into a hydrophilic surface having a water contact angle of 10° or less, wherein the surface which becomes hydrophilic serves as a non-printing image portion and the remaining hydrophobic surface serves as a printing image portion.

[0027]

The printing plate material is one which possesses the same effects as the invention recited in claim 9. Accordingly, the printing plate material is one which can accommodate to digitalization of printing processes.

[0028]

The printing plate material as recited in claim 11 is a printing plate material recited in any of claims 1 to 10, wherein one or two or more of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+} is contained as an oxide. Furthermore, the printing plate material as recited in any of claim 12 is one wherein one or two or more of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+} is contained as an oxide compound with titanium. In either case, when the coat layer surface is irradiated, the hydrophilic image phenomenon of the part irradiated thereby is accelerated, making possible faster plate preparation. That is, one or two or more of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+} is in an ion state, and even if it/they were in either an oxide state or in an oxide state combined with titanium.

[0029]

As recited in claim 13, the method for renewing a printing plate material comprising a substrate on the surface of which a coat layer containing a titanium oxide photocatalyst and one or two or more of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+} is formed directly or with an intermediate layer intervening, comprises at least the steps of cleaning a surface of a coat layer containing a titanium oxide photocatalyst after completion of printing; and then renewing the coat layer containing a titanium oxide photocatalyst.

[0030]

Regarding this, it is clear that the same effect as that derived from claim 7 can be attained.

[0031]

As recited in claim 14, in the method for renewing a printing plate material in which the surface of the coat layer is reconverted to become a hydrophobic surface as

recited in any of claims 4 to 7, a step of reconverting the coat layer is performed in a printing machine.

[0032]

Accordingly, when undertaking actual printing, there is no sandwiching discontinuance of continuous printing operations which conceivably is generally pursuant during operations related to reconversion.

[0033]

As recited in claim 15, with the method for renewing a printing plate material comprising a substrate, the surface of which comprises a coat layer containing a titanium oxide photocatalyst and at least one or two or more of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+}formed directly or with an intermediate layer intervening, and a coating layer comprising a compound which can be decomposed by irradiation with light having a wavelength at an energy level higher than a band gap energy level of the titanium oxide photocatalyst on the coat layer, the method comprises at least the steps of cleaning an outermost surface including a surface of the coat layer which is hydrophilic in at least one portion thereof; then reforming the coating layer to cause a hydrophobic surface having a water contact angle of 50° or more to emerge; and then irradiating the light onto the coating layer surface.

[0034]

Accordingly, by coating the compound, since the coat layer surface is converted to become hydrophobic, at this time, the printing plate material can be regarded as having gone into an initial state. Furthermore, this essentially means that reuse of the printing plate material becomes possible. Moreover, the abovementioned fact, that is, work of conversion into a hydrophobic property, is substantially just due to the work of coating a compound; thus, the work can be completed swiftly.

[0035]

With the method for renewing a printing plate material as recited in claim 16 the method of renewing the printing plate material recited in claim 15 is performed in a printing machine.

[0036]

Accordingly, when printing occurs, there is no sandwiching discontinuance of

continuous printing operations which conceivably is generally pursuant during operations related to conversion into a hydrophobic property.

[0037]

[Embodiments of the Invention]

(First Embodiment)

Hereafter, embodiments of the present invention will be described with reference to the attached drawings. Fig. 1 is a cross-sectional view showing the printing plate material according to the present embodiment. In Fig. 1, a substrate 1 is composed of aluminum. To use aluminum as a printing plate material is a common mode but the present invention is not limited thereto.

[0038]

An intermediate layer 2 is formed on the surface of the substrate 1. The material which can be used for the intermediate layer 2 includes, for example, silicon-based compounds such as silica (SiO_2), silicone resins, and silicone rubbers. Of these, in particular, there are used silicone resins such as silicone alkyd, silicone urethane, silicone epoxy, silicone acrylic, and silicone polyester. The intermediate layer 2 is formed in order to ensure attachment of and secure the adhesion of the substrate 1 and a coat layer 3 described hereinbelow. That is, firmly bonding the substrate 1 and the intermediate layer 2 and also the coat layer 3 and the intermediate layer 2 allows the bond strength of the substrate 1 to the coat layer 3 to be secured.

[0039]

The coat layer 3, which contains a titanium oxide photocatalyst, is formed on the intermediate layer 2. The surface of the coat layer 3 is hydrophobic in an initial state of the printing plate as prepared, and a portion which is hydrophilic emerges by irradiating the portion with ultraviolet rays. This property is attributable to the property of the above titanium oxide photocatalyst. This will be explained in detail later on. In addition, in the coat layer 3, a metal other than titanium such as at least one or two or more of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+} is incorporated as an ion, an oxide, or a compound oxide with titanium, in order to promote the hydrophilization phenomenon by irradiation of ultraviolet light due to the interaction between the titanium oxide photocatalyst and the other metal.

[0040]

In addition, the coat layer 3 may contain one or more of the following substances in order to improve the property of conversion from hydrophilicity to hydrophobicity or to increase the strength of the coat layer 3 or the adhesion of it to the substrate 1. Examples of the substances include silica-based compounds such as silica, silica sol, organosilane, and silicone, metal oxides or metal hydroxides containing a metal such as zirconium or aluminum, fluorine-containing resins. Taking into consideration high oxidizing power of the titanium oxide photocatalyst, the coat layer 3 is preferably composed of an inorganic compound or compounds from the viewpoint of preventing the coat layer 3 from deterioration.

[0041]

Titanium oxide photocatalysts per se include anatase types and rutile types having different crystal structures, respectively. In the present embodiment, either of them can be utilized. To enable high definition printing by increasing the resolution of the image to be written on a printing plate, and to enable the formation of the coat layer 3 in a small thickness, the titanium oxide photocatalyst preferably has a particle diameter of 0.1 μm or less.

[0042]

As for the titanium oxide photocatalyst, specific examples thereof which are commercially available and can be used in the present embodiment include ST-01, ST-21, their processed products ST-K01 and ST-K03, water dispersed type STS-01, STS-02 and STS-21, all produced by Ishihara Sangyo Kaisha, Ltd.; SSP-25, SSP-20, SSP-M, CSB, and CSB-M, and paint type LAC TI-01, produced by Sakai Chemical Industry Co., Ltd.; ATM-100, ATM-600, and ST-157 produced by TAYCA Corporation. However, it is needless to say that the present invention can be practiced with titanium oxide photocatalysts other than the above.

[0043]

It is preferred that the coat layer 3 have a thickness in the range of 0.01 to 10 μm. This is because too small a film thickness makes it difficult to utilize the above-described properties sufficiently, whereas too large a film thickness tends to lead to cracking of the coat layer 3, thereby causing a decrease in durability. The cracking is observed remarkably when the film thickness exceeds 50 μm, so that it is necessary to note that an upper limit

of the film thickness is 50 μm, if the above range is to be realized. In a general mode, in practice, the film thickness is on the order of 2 to 3 μm.

[0044]

The methods for forming the coat layer 3 include:

a method of coating a titanium oxide photocatalyst sol containing at least one or two or more of the salts of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+};

a method of coating a mixture of a titanium oxide photocatalyst sol and at least one or two or more of the oxides of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+};

a method of coating a mixture of a titanium oxide photocatalyst sol and at least one or two or more of the alkoxides of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+};

a method of coating a mixture of an organic titanate and at least one or two or more of the alkoxides of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+};

a method of vapor deposition using a pellet comprising a mixture of at least one or two or more of the oxides of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+} and a titanium oxide photocatalyst in a predetermined mixing ratio; and

a method of ion injection of at least one or two or more of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+} into a titanium oxide photocatalyst layer formed by a vapor deposition method.

[0045]

In this case, for example, when a coating method is adopted, the coating liquid used therein may contain solvents, crosslinking agents, surfactants, etc. The coating liquid may be either of a room temperature drying type or of a heat drying type. It is more preferable to adopt the latter since it is more advantageous for increasing the durability of printing plate to increase the strength of the coat layer 3 by heating.

[0046]

Hereafter, the operation and effect of the printing plate material having the above construction will be described. First, in an initial state of the printing plate material as prepared, the surface of the coat layer 3 is adjusted to have hydrophobicity in terms of a water contact angle of 50° or greater as shown in Fig. 1. In this connection, a more preferred state may be obtained by adjustment such that the above contact angle is 80° or more. In this state, as can be seen from Fig. 1, it is difficult for water to adhere to the surface of the coat layer 3, that is, the surface of the coat layer 3 is in a state where its

water repellency is very high. Expressing it the other way around, it can be said that there emerges a state where a printing ink can readily adhere to the surface of the coat layer 3.

[0047]

The expression "an initial state of the printing plate material as prepared" can be interpreted as meaning the time of initiation in an actual printing process. More specifically, it indicates a state where, for any given image, digitized data thereof are already provided and an image from the data is being written onto the printing plate material. However, the stage at which the digitized data are provided may be after the hydrophobization treatment in respect of the surface of the coat layer 3 as described later on and the statement just above should not be construed in a strict sense. That is, when the "initial state of the printing plate material as prepared" is defined as the "time of initiation in an actual printing process," such should be interpreted in a broad sense.

[0048]

Next, the surface of the coat layer 3 in the above state is irradiated with ultraviolet rays as shown in Fig. 2. The irradiation with ultraviolet rays is performed in accordance with digital data on the above-described image and so as to correspond to the data. The ultraviolet rays as used herein refer to light having a wavelength having an energy higher than the band gap energy of the titanium oxide photocatalyst, more specifically, ultraviolet rays containing light having a wavelength of 400 nm or less.

[0049]

Upon irradiation with the ultraviolet rays, the surface of the coat layer 3 becomes hydrophilic as shown in Fig. 2. This is attributable to the effect of the titanium oxide photocatalyst. As a result, the region irradiated with ultraviolet rays is in a state where its water contact angle is 10° or less. This state is just in a relationship opposite to the state of the hydrophobic surface earlier described. That is, water spreads on the surface of the coat layer 3 almost in the form of a film but it is impossible for printing inks to adhere to the surface.

[0050]

The method for generating the hydrophilic portion based on the above image can be practiced without difficulty since it is only necessary to control the region which is irradiated with ultraviolet rays based on the above digital data of the image concerned.

That is, unlike conventional PS plates whose hydrophobic portion is formed by hardening a photosensitive resin, it can be said that the printing plate material of the present embodiment is adaptable to the digitization of printing process without difficulty.

[0051]

In this connection, the mechanism in which the titanium oxide photocatalyst is rendered hydrophilic by irradiation with ultraviolet rays is roughly presumed as follows. When the titanium oxide photocatalyst is hydrophobic, oxygen O^{2-} is bonded in the form of a bridge between Ti^{4+} ions on the surface thereof as shown in Fig. 3(a). Upon irradiation of this with ultraviolet rays, the bridge-like O^{2-} is converted into an O atom, which is eliminated from the surface and the two electrons released from the eliminated O^{2-} reduce two adjacent Ti^{4+} to form (Ti^{3+})s as shown in Fig. 3(b). Then, water molecules in the air are adsorbed onto the oxygen deficient portion to form hydroxyl groups. These hydroxyl groups further adsorb water molecules from the air and thereby a layer of hydroxyl groups is formed on the surface of the coat layer, resulting in hydrophilicity. Thus, the phenomenon of hydrophilization of the titanium oxide photocatalyst starts from the reduction process of Ti^{4+} under irradiation with ultraviolet rays. Addition of at least one or two or more of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+} into a titanium oxide photocatalyst layer in a small amount promotes the reduction process of Ti^{4+}. The addition amount is 0.05 to 5% by weight, and preferably 0.1 to 1% by weight. This is because, if this amount is too small, the effect of promoting the reduction process of Ti^{4+} is insufficient while, if it is too large, the inherent function of the titanium oxide photocatalyst is damaged.

[0052]

When the treatment thus far is over, a hydrophobic printing ink is coated onto the surface of the coat layer 3. Then, for example, a printing plate material as shown in Fig. 4 is prepared. In Fig. 4, the hatched portion is a portion where the above hydrophilization treatment has not been performed, that is the hydrophobic portion, and hence indicates a printing image portion 4 where a printing ink is adhered. The remaining background portion, that is, the hydrophilic portion, repels the printing ink and hence indicates a non-printing image portion where no adhesion of the printing ink has occurred. Emergence of a picture pattern in this manner allows the surface of the coat layer 3 to function as a master plate.

[0053]

Thereafter, a usual printing process is practiced and completed. Hereafter, two modes will be described.

[0054]

As a first mode, a printing plate material which has passed through a usual printing process is provided and on the coat layer 3 thereof one of irradiation with a flux of energy of light, heat, sonic wave, electron beam, etc., is performed, and surface treatment with a chemical substance such as a solution of chemical, a gas, or a catalyst, that is, a chemical conversion treatment, is performed. These may be performed simultaneously or separately. Practicing such an operation (treatment for removing hydroxyl groups in the hydrophilic state as shown in Fig. 3) causes the hydrophilic portion of the coat layer 3 to become hydrophobic again as indicated by curve A in Fig. 5. Fig. 5 is a graph plotting time in the horizontal axis vs. water contact angle in the the vertical axis, illustrating the change in water contact angle concerning a certain point on the surface of the coat layer 3 with the passage of time.

[0055]

Usually, the hydrophilization-treated titanium oxide photocatalyst has a property that its hydrophilized portion when stored in the dark naturally shifts to gradually become a surface having hydrophobicity (cf. curve B in Fig. 5). This shift is completed usually in a week to a month or so and, thereafter, the entire surface becomes hydrophobic again. Upon utilizing the hydrophobic performance and hydrophilic performance, efforts are generally made to maintain hydrophilicity. That is, it is a conventional way of thinking and general to make efforts to prolong the time required for the shift from hydrophilicity to hydrophobicity which takes a week to a month or so.

[0056]

In the present embodiment, as described above, the addition of one or two or more of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+} into the titanium oxide photocatalyst layer can increase the rate of hydrophilization when irradiated with ultraviolet rays, and a treatment is practiced which is intended to positively reverse the surface of the coat layer 3 having hydrophilicity to hydrophobicity by irradiation with a flux of energy and by a chemical conversion treatment. Therefore, no effort is made to maintain hydrophilicity, nor is it

necessary to wait for the completion of the shift, which takes a week to a month or so, but it is intended to try to have the shift from hydrophilicity to hydrophobicity occur in a very short period of time.

[0057]

In the present embodiment, quick completion of the reversion to hydrophobicity enables returning to the above-described "initial state of the printing plate material as prepared" again. That is, the surface of the coat layer 3 has hydrophobicity such that the printing ink can be adhered to the entire surface of the coat layer. Irradiation of the surface with ultraviolet rays again enables preparation of a new master plate for printing. In short, the printing plate material of the present embodiment allows for its recycling, in other words repeated use.

[0058]

Hereafter, another mode will be described. In this mode, first the surface of printing plate is wiped, that is, the ink, dampening water, etc., that are adhered to the surface of the coat layer 3 are wiped off. In other words, cleaning of the surface of the coat layer 3 is performed. Thereafter, the coat layer 3 containing the titanium oxide photocatalyst is formed again to create a new hydrophobic surface. The renewal of the coat layer 3 is practiced by using the above-described sol coating method, organic titanate method, vapor deposition method or the like appropriately. Practically, it is preferable to select the coating method. In this case, specifically, methods such as spray coating, blade coating, dip coating, roll coating, may be used. The used coat layer may be removed before the coat layer 3 is renewed. Desirably, the renewed coated layer 3 has a film thickness of 0.05 μm or more. If the film thickness exceeds 20 μm, care must be taken since cracks tend to occur.

[0059]

From this it follows that in this mode too, as in the mode described with reference to Fig. 5, it is obvious that the printing plate can be used repeatedly or recycled as shown in Fig. 6. That is, since the coat layer 3 which provides a surface having hydrophobicity is created again, it can be said that the printing plate material at that point in time is reversed to the "initial state of the printing plate material as prepared." Hence, irradiation of this surface with ultraviolet rays enables preparation of a new master plate.

[0060]

Hereafter, a more specific example relating to preparation and printing of a printing plate material which the present inventors have confirmed will be described. First, a substrate made of aluminum having a size of a post card and a thickness of 0.3 mm was provided. On this, a primer, LAC PR-01 manufactured by Sakai Chemical Industry Co., Ltd., was coated and dried. After the drying, the thickness of the primer layer was 1.4 μm. The primer layer corresponds to the intermediate layer 2 in Fig. 1. Thereafter, a titanium oxide photocatalyst coating agent LAC TI-01 manufactured by Sakai Chemical Industry Co., Ltd., containing NiO sol in an amount of 0.2% by weight as Ni^{2+} based on titanium oxide was coated thereon and dried at 100°C to form the coat layer 3 containing the titanium oxide photocatalyst having a thickness of 1.0 μm. Measurement of the printing plate material for a water contact angle on the surface of the coat layer 3 using a CA-W type contact angle meter manufactured by Kyowa Kaimen Kagaku Co., Ltd. gave a water contact angle of 95°, thus exhibiting hydrophobicity sufficient as a printing image portion.

[0061]

Next, the printing plate material was set onto a SAN OFF-SET 220E DX type card printing machine manufactured by SAN PRINTING MACHINES CO. Printing was performed on AIBESUTO paper with HYECOO B Red MZ ink manufactured by Toyo Ink Manufacturing Co., Ltd. and dampening water, a 1% solution of LITHOFELLOW manufactured by Mitsubishi Heavy Industries, Ltd., and at a printing speed of 2500 sheets/hour. As a result, the ink adhered to the entire surface of the printing plate material (that is, the surface of the coat layer 3, hereafter the same), and a red image having the same size as the printing plate material and a uniform density could be printed on the paper.

[0062]

With the printing plate material for which coating of the coat layer 3 was completed, i.e., the printing plate material in an initial state of the printing plate material as prepared, the surface of the coat layer 3 was irradiated with ultraviolet rays at an illuminance of 40 mW/cm^2 for 1 minute. Immediately thereafter, the water contact angle was measured using the above-described CA-W type contact angle meter, and a water contact angle of 4° was obtained, thus exhibiting hydrophilicity sufficient as a non-printing

image portion. Using this printing plate material, printing was performed in the same manner as described above. As a result, no ink adhered to the printing plate and no image could be printed on the paper. In the case of the printing plate material prepared without addition of NiO sol, it took 5 minutes before a water contact angle of 10° or less could be reached as a result of irradiation with ultraviolet rays.

[0063]

In the same manner as in the foregoing, in the printing plate material in an initial state of the printing plate material as prepared, a central part thereof was masked by black paper in the form of a square of 2 cm long on each side. The unmasked portion was irradiated with ultraviolet rays at an illuminance of 40 mW/cm^2 for 1 minutes and immediately thereafter, the water contact angle of the ultraviolet irradiated portion was measured using a CA-W type contact angle meter to obtain a water contact angle of 5°, thus exhibiting hydrophilicity sufficient as a non-printing image portion. Using this printing plate material, printing was performed in the same manner as described above. As a result, no ink adhered to the portion of the printing plate which was irradiated with ultraviolet rays and no image could be printed on the paper and a red image of a square of 2 cm long on each side corresponding to the portion of the printing plate material masked could be printed on the paper.

[0064]

Next, two examples relating to the renewal of a printing plate material will be described below. First, a printing plate material from which the ink and dampening water adhered to the surface thereof were wiped off was placed in a dark room so that it could not be exposed even to weak ultraviolet rays. The dark room was kept in a nitrogen atmosphere. The surface of the printing plate material was subjected to a heat treatment at 180°C for 5 minutes. As a result, the water contact angle of the surface of the printing plate material on which these treatments were completed was measured using CA-W type contact angle meter, and a water contact angle of 93° was obtained, which indicated that the surface was returned to a hydrophobic surface as before irradiation with ultraviolet rays.

[0065]

Next, in a state where the printing plate was set onto a card printing machine, the ink and dampening water adhered to the surface of the printing plate were wiped off and

the above-described titanium oxide photocatalyst coating agent LAC TI-01 was coated onto the surface of the printing plate by roll coating. Thereafter, it was dried in hot air at 120°C to renew the coat layer 3 containing the titanium oxide photocatalyst. Using this renewed plate, printing was performed in the same manner as in the printing before the renewal. As a result, the ink adhered to the entire surface of the printing plate material and a red image having the same size as the printing plate and a uniform density could be printed on the paper.

[0066]

The above printing was performed using a printing machine 10 as shown in Fig. 11. Specifically, the printing machine 10 comprises a coating apparatus 12, a blanket cylinder 13, a plate cleaning apparatus 14, a writing apparatus 15, an inking roller 16, and a drying apparatus 17 around the plate cylinder 11 in the center. The printing plate material is arranged wound around the plate cylinder 11.

[0067]

In the printing machine 10, the process for renewing the printing plate after completion of the printing as described above was performed as follows. First the plate cleaning apparatus 14 was brought into contact with the plate cylinder 11 and the ink and dampening water adhered to the surface of the printing plate were wiped off. Thereafter, the plate cleaning apparatus 14 was released from the plate cylinder 11 and the coating apparatus 12 was brought into contact with the plate cylinder 11. By so doing, the coat layer 3 was being renewed on the printing plate material. Thereafter, the coating apparatus 12 was released from the plate cylinder 11, followed by operating the drying apparatus 17 to evaporate the solvents, etc., contained in the coat layer 3. Then, an image was written on the renewed surface of the coat layer 3 with ultraviolet rays emitted by the writing apparatus 15 based on digital data of the image provided in advance. After completion of the above steps, the inking roller 16 and the blanket cylinder 13 were brought into contact with the plate cylinder 11. Then paper 18 was fed so as to make contact with the blanket cylinder 13 and to be carried in the direction of the arrow as shown in Fig. 7 so that continuous printing could be performed.

[0068]

As described above, the printing plate material of the present embodiment makes

the best of the property of titanium oxide photocatalyst, i.e., its property of converting hydrophobicity to hydrophilicity, thereby enabling its recycling and considerably decreasing the amount of printing plate material to be disposed of after use. Therefore, the costs incurred by printing plate materials can be decreased to a greater extent accordingly. Since writing an image onto the printing plate materials can be practiced from the digital data on the image directly by light (ultraviolet rays), adaptation to the digitization of printing process is achieved so that reduction in time and saving costs can be made to a greater extent accordingly. In addition, it can increase the rate of hydrophilization under irradiation with ultraviolet rays by addition therein of one or two or more of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+} in the form of ions, oxides, or composite oxides with titanium so that the time required for writing of images to the printing plate material can be reduced.

[0069]

Since reconversion of printing plate materials and practice of renewal of the coat layer 3 can be performed in a printing machine, speeding up of the printing operation can be realized. In the above examples, writing of images onto the surface of the coat layer 3 was performed in a printing machine and therefore operation can be practiced more speedily.

[0070]

In the present embodiment, the intermediate layer 2 was provided between the substrate 1 and the coat layer 3. However, the present invention is not limited thereto. That is, the intermediate layer 2 does not have to be provided. This is because the major essential features of the present invention are not harmed by the absence of the intermediate layer 2 as will be apparent from the explanation thus far made.

[0071]

In regard to the renewal of printing plates, the above explanation was made using embodiments or examples involving freshly coating the coat layer 3. On this point, the following supplemental explanation will be made. That is, similar effects can be obtained by such a method as to scrape off the superficial portion of the thus far used coat layer 3 but not newly coating the coat layer 3 after the completion of the printing. That is, scraping off the entire superficial portion of the coat layer 3 after completion of the printing as shown in Fig. 2, for example, results in removal of the hydrophilic portion by a

single effort and instead a new surface of the coat layer 3 hidden therebelow can emerge. Since the new surface of the coat layer 3 exhibits hydrophobicity, it is understandable that such a method can also cause the initial state of the printing plate material as prepared to emerge. The "renewal of the coat layer" as used herein encompasses the idea as described just above in its scope.

[0072]

(Second Embodiment)

Hereafter, a second embodiment of the present invention will be described.

Fig. 7 is a cross-sectional view showing a printing plate material of this embodiment. In Fig. 7, the substrate 21, the intermediate layer 22, and the coat layer 23 are the same as those in the above first embodiment, and therefore detailed explanation thereof is omitted here.

[0073]

On the coat layer 23 is formed a coating layer 24 composed of a compound which can be decomposed by irradiation thereof with light with a wavelength having an energy higher than a band gap energy of the titanium oxide photocatalyst. The surface of the coating layer 24 is adjusted to have hydrophobicity in terms of a water contact angle of 50° or greater as shown in Fig. 7. In this connection, it is a more preferable state if the surface of the coating layer 24 is adjusted to a water contact angle of 80° or more. In this state, as will be understood from Fig. 7, it is difficult for water to adhere to the surface of the coating layer 24, that is, the coating layer 24 has high water repellency. Expressing it the other way around, it can be said that there emerges a state where a printing ink can readily adhere to the surface of the coating layer 24.

[0074]

Hereafter, the operation and effect of the printing plate material having the above construction will be described. First, in an initial state of the printing plate material as prepared, the surface of the coat layer 23 is adjusted to have hydrophobicity in terms of a water contact angle of 50° or greater as shown in Fig. 7. The expressions "an initial state of the printing plate material as prepared" and "adjustment so as to have hydrophobicity" indicate the following situations. First, "adjustment so as to have hydrophobicity" is carried out by forming the coating layer 24 composed of a compound which can be

decomposed by irradiation of the surface of the coat layer 23 with ultraviolet rays and drying it. For this coating can be appropriately adopted a method selected from spray coating, blade coating, dip coating, and roll coating methods. The drying may be performed at room temperature or with heating. When the surface of the coat layer 23 becomes hydrophobic by the "adjustment," it is defined to be "in an initial state of the printing plate material as prepared."

[0075]

The above compound is preferably not only one having the effect of imparting hydrophobicity to the above-described surface, but also one which can be "readily" subject to oxidative decomposition reaction by irradiation with ultraviolet rays. Specifically, there can be cited, for example:

(1) alkoxysilanes such as trimethylmethoxysilane, trimethylethoxysilane, dimethyldiethoxysilane, methyltrimethoxysilane, tetramethoxysilane, methyltriethoxysilane, tetraethoxysilane, methyldimethoxysilane, octadecyltrimethoxysilane, and octadecyltriethoxysilane;

(2) chlorosilanes such as trimethylchlorosilane, dimethyldichlorosilane, methyltrichlorosilane, methyldichlorosilane, and dimethylchlorosilane;

(3) silane coupling agents such as vinyltrichlorosilane, vinyltriethoxysilane, γ-chloropropyltrimethoxysilane, γ-chloropropylmethyldichlorosilane, γ-chloropropylmethyldimethoxysilane, γ-chloropropylmethyldiethoxysilane, and γ-aminopropyltriethoxysilane;

(4) silazanes such as hexamethyldisilazane, N,N'-bis(trimethylsilyl)urea, N-trimethylsilylacetamide, dimethyltrimethylsilylamine, and diethyltrimethylsilylamine;

(5) fluoroalkylsilane such as perfluoroalkyltrimethoxysilane;

(6) silicone oils of the type of dimethyl hydrogen polysiloxane;

(7) fatty acids such as lauric acid, myristic acid, palmitic acid, stearic acid, and oleic acid;

However, it is needless to say that the present invention is not limited to these compounds. In addition, these compounds may of course be diluted with a solvent when used if necessary.

[0076]

The expression "an initial state of the printing plate material as prepared" in general can be interpreted as meaning the time of initiation in an actual printing process. That is, it indicates a state where, for any given image, digitized data thereof are already provided and an image from the data is being written onto the printing plate material. However, the stage at which the digitized data are provided may be after the hydrophilization treatment with respect to the surface of the coat layer 23 as described later on and the statement just above should not be construed in a strict sense. That is, when the "initial state of the printing plate material as prepared" is defined as the "time of initiation in an actual printing process," such should be interpreted in a broad sense.

[0077]

Next, the surface of the coating layer 24 in the above state is irradiated with ultraviolet rays as shown in Fig. 8. The irradiation with ultraviolet rays is performed in accordance with digital data on the above-described image and so as to correspond to the data. The ultraviolet rays as used herein refer to light having a wavelength having an energy higher than the band gap energy of the titanium oxide photocatalyst, more specifically, ultraviolet rays containing light having a wavelength of 400 nm or less.

[0078]

The irradiation with ultraviolet rays decomposes the compound constituting the coating layer 24 as also shown in Fig. 8, causing the surface of the coat layer 3 to emerge and converting the surface to have hydrophilicity. This is attributable to the effect of the titanium oxide photocatalyst. Since the decomposition of the compound proceeds by the inherent catalytic effect of the titanium oxide photocatalyst, it is completed very quickly. This puts the region of the surface of the coat layer 3 irradiated with ultraviolet rays into a state of having a water contact angle of 10° or less. This state is exactly opposite to the state of the hydrophobic surface in the coating layer 24 described earlier. That is, water spreads on the surface of the coat layer 23 almost in the form of a film, whereas it is impossible for a printing ink to adhere on the surface thereof.

[0079]

Description of the mechanism by which the titanium oxide photocatalyst is hydrophilized is omitted here since it is already described in the first embodiment, however, it should be added that in the present invention, the hydrophilization of the

titanium oxide photocatalyst is promoted by addition of at least one or two or more of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+} into the coat layer containing the titanium oxide photocatalyst in a small amount.

[0080]

When the treatment thus far is over, a hydrophobic printing ink is coated onto the surface of the coating layer 24 or the hydrophilization treated coat layer 23. Then, for example, a printing plate material as shown in Fig. 9 is prepared. In Fig. 9, the hatched portion is a portion where the above hydrophilization treatment has not been performed, that is the hydrophobic portion or a portion where the coating layer 24 remains and hence indicates a printing image portion where printing ink is adhered. The remaining non-imaged portion, that is, the hydrophilic portion or the portion where the surface of the coat layer 23 emerges, repels the printing ink and hence indicates a non-printing image portion where no adhesion of the printing ink has occurred. Emergence of a picture pattern in this manner allows the the printing plate material to function as a master plate.

[0081]

Thereafter, usual printing process is practiced and completed. Hereafter, two examples will be described. On the printing plate material, after completion of the printing, a coating layer 24 composed of the above-described compound is formed again. Therefore, the printing plate material is reversed to the "initial state of the printing plate material as prepared" in a stage where the coating is completed. That is, on the surface of the coat layer 23 at this point in time, the coating layer 24 which allows adhesion of a printing ink onto its entire surface is formed and has hydrophobicity. Irradiation of the surface with ultraviolet rays again enables preparation of a new master plate for printing. In short, the printing plate material of the present embodiment allows for its recycling, in other words, repeated use.

[0082]

Fig. 10 is a graph illustrating in summary what is explained above. This is a graph plotting time in the horizontal axis vs. water contact angle in the the vertical axis, illustrating succession in water contact angle (a hydrophobic state or a hydrophilic state) on the surface of the printing plate material of the present embodiment with the passage of time. Fig. 10 shows the results obtained with a titanium oxide photocatalyst having an

ability of completing the conversion from hydrophobicity to hydrophilicity although the titanium oxide photocatalyst alone tends to be insufficient in performance relating to hydrophobicity (having a water contact angle of less than 50° before irradiation with ultraviolet rays).

[0083]

In this case, as described above, the surface of the coat layer 23 in the original state has a water contact angle of 20 to 30°, thus exhibiting an insufficient hydrophobic property. Therefore, the surface of the coat layer 23, as it is, is insufficient for use as a printing image portion and cannot be used as a printing plate material. However, the titanium oxide photocatalyst has an ability of being quickly converted to form a hydrophilic surface upon irradiation with ultraviolet rays. Usually, this conversion takes generally about 10 minutes. In this example, however, it can be seen that the conversion is completed in 1 to 2 minutes.

[0084]

Next, the compound is coated onto the surface of the coat layer 23. That is, formation of the coating layer 24 increases the hydrophobicity of the printing plate material to a sufficient state as indicated by point B via point A. That is, adhesion of an ink is made possible so that it can be in a state where it is supplied for use in printing. This is, the "initial state of the printing plate material as prepared" (point B in Fig. 10). To cause the "initial state of the printing plate material as prepared" to emerge, it is substantially sufficient to merely coat the compound as described above, so that obviously, such operation can be completed in a very short time.

[0085]

Thereafter, irradiation with ultraviolet rays is performed to decompose the above compound and convert at least a portion of the surface of the coat layer 23 to a hydrophilic portion. In this case, the conversion from hydrophobicity to hydrophilicity in the titanium oxide photocatalyst can be completed in 1 minute as indicated by curve C in Fig. 10 by three effects. The first one is the effect of using the above-described titanium oxide photocatalyst having a high rate of conversion from hydrophobicity to hydrophilicity, the second one is a speedy completion of the decomposition of the compound by the inherent catalytic effect of the titanium oxide photocatalyst as described above, and the third one is

an increse in the rate of hydrophilization by the addition of at least one or two or more of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+}.

[0086]

To the printing plate material subjected to the above treatment, a printing ink is adhered and actual printing is performed as indicated by straight line D in Fig. 10. Subsequent to completion of the printing, the printing plate material is subjected to treatments such as coating of the compound and irradiation with ultraviolet rays similarly to the above before it can be recycled.

[0087]

As described immediately above, the printing plate material of the present embodiment has an advantage that it can be recycled and, in addition, another advantage that its cycle can be speeded up. That is, according to the above advantages, no excessive time is necessary for realization of imparting either hydrophobicity or hydrophilicity. Therefore, the whole printing process can be completed very quickly.

[0088]

Hereafter, a more specific example relating to preparation and printing of a printing plate material relating to the embodiment which the present inventors have confirmed will be described. First, a coat layer 23 is formed in a manner similar to that in the first embodiment. Further, on the surface of the coat layer 23 was coated by roll coating a hydrophobization treating solution prepared by diluting octadecyltrimethoxysilane (trade name: TSL8185) manufactured by Toshiba Silicone Co., Ltd. with ethanol to a concentration of 3% by weight while slowly stirring for 5 minutes and adding 5,000 ppm of formic acid to the resulting solution, followed by slowly stirring again for 5 minutes. This was dried at 100°C to form a coating layer, and the "initial state of the printing plate material as prepared" as explained heretofore repeatedly was caused to emerge.

[0089]

The printing plate material coated with the above hydrophobization treatment solution (i.e., an ethanol solution of octadecyltrimethoxysilane and formic acid) and dried was masked in its central part by black paper in the form of a square of 2 cm long on each side. The unmasked portion was irradiated with ultraviolet rays at an illuminance of 40 mW/cm^2 for "1 minute" and immediately thereafter, the water contact angles of the

masked portion and ultraviolet irradiated portion were measured using a CA-W type contact angle meter manufactured by Kyowa Kaimen Kagaku Co., Ltd. to obtain water contact angles of the masked portion and ultraviolet irradiated portion of 82° and 0 to 2°, respectively. Thus the masked portion exhibits hydrophobicity sufficient for use as a printing image portion while the ultraviolet irradiated portion exhibits hydrophilicity sufficient for use as a non-printing image portion.

[0090]

The printing plate material was set onto a SAN OFF-SET 220E DX type card printing machine, manufactured by SAN PRINTING MACHINES CO. Printing was performed on AIBESUTO paper with an ink HYECOO B Red MZ manufactured by Toyo Ink Manufacturing Co., Ltd. and dampening water, a 1% solution of LITHOFELLOW manufactured by Mitsubishi Heavy Industries, Ltd., at a printing speed of 2500 sheets/hour. As a result, no ink adhered to the ultraviolet irradiated portion of the surface of printing plate material while a red image in the form of a square having a length of 2 cm on each side was printed on the paper.

[0091]

Subsequently, after printing was finished and the ink and the dampening water were wiped off thoroughly, the hydrophobization treatment solution was coated onto the printing plate material in the same manner as described above and dried. Further, the central portion of the surface of printing plate material was masked by a circular black paper having a diameter of 2 cm and the obtained printing plate material was irradiated with ultraviolet rays at an illuminance of 40 mW/cm^2 for 1 minute to form a sample. This treatment corresponds to the treatment to be practiced on recycling printing plate materials. In this case too, the ultraviolet irradiated portion had a water contact angle of 0 to 2°, showing sufficient hydrophilicity for use as a non-printing image portion and in actual printing, a red image could be printed on the paper in the form of a circle having a diameter of 2 cm corresponding to the masked portion of the printing plate material.

[0092]

Next, in a state where the printing plate was set onto a card printing machine, the ink and dampening water adhered to the surface of the printing plate were wiped off and the above-described hydrophobization treatment solution was coated onto the surface of

printing plate by roll coating. Thereafter, it was dried in hot air at 120°C to render hydrophobic the surface of the printing plate material. The hydrophobized printing plate material in its substantially central portion was masked by black paper in the form of a regular triangle, 2 cm long on each side, and the non-masked portion was irradiated with ultraviolet rays at an illuminance of 40 mW/cm^2 for 1 minute. Using this printing plate material, printing was performed in the same manner as in the printing as described above. As a result, no ink adhered to the ultraviolet irradiated portion of the surface of printing plate material while a red image in the form of a regular triangle having a length of 2 cm on each side could be printed on the paper.

[0093]

The above printing was performed using the printing machine 10 as shown in Fig. 11 and described in the first embodiment. Specifically, the printing machine 10 comprises a coating apparatus 12, a blanket cylinder 13, a plate cleaning apparatus 14, a writing apparatus 15, an inking roller 16, and a drying apparatus 17 around the plate cylinder 11 in the center. The printing plate material is arranged wound around the plate cylinder 11.

[0094]

In the printing machine 10, the actual process for recycling the printing plate material after the printing is performed as follows. First, the plate cleaning apparatus 14 was brought into contact with the plate cylinder 11 and the ink and dampening water adhered to the outermost surface of the printing plate, i.e., the printing area, were wiped off. Thereafter, the plate cleaning apparatus 14 was released from the plate cylinder 11 and the coating apparatus 12 was brought into contact with the plate cylinder 11. By so doing, the hydrophobization treatment solution was coated on the surface of the plate cylinder 11. Thereafter, the coating apparatus 12 was released from the plate cylinder 11, followed by operating the drying apparatus 17 to evaporate the hydrophobization treatment solution. Then, an image was written onto the renewed surface of the coat layer 3 with ultraviolet rays emitted by the writing apparatus 15 based on digital data of the image provided in advance. After completion of the above steps, the inking roller 16 and the blanket cylinder 13 were brought into contact with the plate cylinder 11. Then paper 18 was fed so as to make contact with the blanket cylinder 13 and to be carried in the direction of the arrow as shown in Fig. 11 so that continuous printing could be performed.

[0095]

As described above, the printing plate material of the present embodiment makes the best of the property of titanium oxide photocatalyst, i.e., its property of converting hydrophobicity to hydrophilicity, thereby enabling its recycling and considerably decreasing the amount of printing plate material to be disposed of after use. Therefore costs incurred by printing plate materials can be decreased to a greater extent accordingly. Since writing an image onto the printing plate materials can be practiced from the digital data on the image directly by light (ultraviolet rays), adaptation to the digitization of printing process is achieved so that reduction in time and saving costs can be made to a greater extent accordingly.

[0096]

As referred to above, in the case of the present embodiment where recycling of printing plate materials is achieved by formation of the coating layer 24 composed of the compound, speeding up of the whole printing process is made possible. It makes a great contribution to this that the decomposition of the compound is promoted by the inherent catalytic effect of the titanium oxide photocatalyst so that it can be completed quickly. Further, utilization of the titanium oxide photocatalyst which has a high rate of conversion from hydrophobicity to hydrophilicity and incorporation of at least one or two or more of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+} in the form of ions, oxides, or composite oxides with titanium contribute to a further speeding up of the conversion.

[0097]

In addition, the treatment contemplated for the achievement of the recycling of printing plate materials can be performed in the printing machine so that speeding up of the printing operation can be realized. In the above example, writing of images to the coating layer 24 has also been performed in a printing machine, and thereby more speedy operation can be realized.

[0098]

In the present embodiment, the intermediate layer 22 was provided between the substrate 21 and the coat layer 23. However, the present invention is not limited thereto. That is, the intermediate layer 23 does not have to be provided. This is because the major essential features of the present invention are not harmed by the absence of the

intermediate layer 23 as will be apparent from the explanation thus far made.

[0099]

[Effects of the Invention]

As explained above, the printing plate material recited in claim 1 is constituted such that conversion from hydrophobicity to hydrophilicity is made possible by forming on the surface of a substrate a coat layer containing a titanium oxide photocatalyst either directly or with an intermediate layer intervening, and by irradiation of the surface with light (below, simply, ultraviolet ray) having a wavelength at an energy level higher than a band gap energy level of the titanium oxide photocatalyst. Accordingly, a function as a printing plate material is exhibited by the use of a hydrophobic part as an image part and a hydrophilic part as a non-image part. Furthermore, by blending in one or two or more of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+} in an ionic, oxide, or oxide compounded with titanium state, the speed of y providing an intermediate layer between the substrate and the coat layer in this case, sufficient adhesion of both is ensured.

[0100]

The printing plate material of claim 2 can achieve the state wherein the entire printing plate surface becomes an image part in the initial state, because the surface of the coat layer has hydrophobicity in terms of a water contact angle of at least 50° or greater in its initial state during preparation of a printing plate. In other words, when irradiation occurs such that when an image is copied onto the coat layer surface, the image can be made to arise and the printing plate material can be used as a master plate. Furthermore, by irradiation with light having a wavelength at an energy level higher than a band gap energy level of the titanium oxide photocatalyst, the portion of the coat layer surface thus irradiated can be used as a non-image portion. Moreover, the irradiation of ultraviolet radiation can be made to occur based on digital data that conform to the image to be printed. Accordingly, the printing plate material according to the present invention is one which accommodates digitalized printing processes, thus allowing printing time to be greatly shortened and costs to be reduced.

[0101]

The printing plate material of claim 3 also allows conformity with digitalization of printing processes, thus allowing printing time to be greatly shortened and costs to be

reduced.

[0102]

The printing plate material according to claim 4 allows reuse of printing plate material because the surface thereof is converted to become hydrophobic by the irradiation of an energy flux onto the coat layer being hydrophilic in at least one portion of the surface thereof. Accordingly, unlike conventional printing plate materials, there is no need for disposal upon completion of printing, thus related costs can be reduced.

[0103]

The printing plate material of claim 5 provides for the reuse of printing plates by the carrying out of a chemical treatment instead of the energy flux radiation. Accordingly, it is clear that the same effect as that of claim 4 can be attained.

[0104]

The printing plate material of claim 6 provides for the reuse of printing plates by a combined carrying out of a chemical treatment with the energy flux radiation. By this, too, the same benefits according to claim 4 can be enjoyed. Furthermore, in the present invention, since a plurality of methods may be used, as mentioned above, conversion from hydrophilicity to hydrophobicity can be completed swiftly.

[0105]

The printing plate material of claim 7 attempts to achieve renewal of a printing plate material directly by renewal of the coat layer. Although the methods differ, it is clear that the same effects as those disclosed in claim 4 can be obtained.

[0106]

Due to the function of the compounds which are decomposed by irradiation with light having a wavelength at an energy level higher than a band gap energy level of the titanium oxide photocatalyst, and the titanium oxide photocatalyst, the printing plate material according to claim 8 allows the separation of regions, one being hydrophobic and the other being hydrophilic. Furthermore, hydrophilic phenomena are facilitated by the inclusion of one or two or more of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+} within the coat layer, thus allowing faster preparation of plates.

[0107]

According to claims 9 and 10, in claim 8, the same effects as claims 2 and 3 can be

attained.

[0108]

It is clear that the methods recited in claims 13 and 15 for renewing a printing plate material can attain the same applicable effects which will have the same qualities as the applicable effects derived from claim 8.

[0109]

The renewal methods recited in claims 14 and 16 do not sandwich a discontinuance of continuous printing operations which conceivably is generally pursuant during the operations, because renewal and reconversion of the coat layer surface are performed in a printing machine. Accordingly, continuous printing operations can be implemented and printing operations can be made more rapid. Moreover, it goes without saying that the present invention can enjoy the benefits of plate reuse at the same time.

[Brief Description of the Drawings]

Fig. 1 is a cross-sectional view showing the construction of a printing plate material of the first embodiment. This figure also indicates the state in which the surface of the coat layer is hydrophobic.

Fig. 2 is a cross-sectional view showing a printing plate material of which a surface of the coat layer is hydrophilic.

Fig. 3 is an illustrative diagram illustrating the conversion from hydrophobicity to hydrophilicity in a titanium oxide photocatalyst.

Fig. 4 is a perspective view showing an example of an image(printing image portion) made on a surface of the coat layer and its background (non-printing image portion).

Fig. 5 is a graph illustrating the state of conversion from hydrophobicity to hydrophilicity of a surface of the coat layer with the passage of time.

Fig. 6 is a graph illustrating the state of conversion from hydrophobicity to hydrophilicity of a surface of the coat layer with the passage of time in a mode different from that shown in Fig. 5.

Fig. 7 is a cross-sectional view showing the construction of a printing plate material of the second embodiment. This figure also indicates the state where a surface of the coat layer is hydrophobic.

Fig. 8 is a cross-sectional view showing a printing plate material in which the surface of the coat layer is in a hydrophilic state.

Fig. 9 is a perspective view showing an example of an image (printing image portion) made on a surface of the coat layer and its background (non-printing image portion).

Fig. 10 is a graph illustrating the state of conversion from hydrophobicity to hydrophilicity of a surface of the coat layer with the passage of time.

Fig. 11 is an illustrative diagram illustrating one example of the construction of a printing machine.

[Brief Description of the Reference Symbols]

1, 21 substrate

2, 22 intermediate layer

3, 23 coat layer

24 coating layer

10 printing machine

[Document Type] Abstract

[Abstract]

[Problems to be Solved by the Invention] To provide a printing plate material which can be adapted to digitization of printing processes and recycled, and a method for renewing the printing plate material.

[Means for Solving the Problems] As the printing plate material, there can be used one which comprises a substrate on the surface of which a coat layer containing a titanium oxide photocatalyst and at least one or two or more of Fe^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and Cu^{2+} is formed. In an initial state of the printing plate as prepared, it the printing plate surface is adjusted to a state where it becomes hydrophobic. This adjusting is carried out by coating the surface with a compound such as octadecyltrimethoxysilane. This surface is irradiated with ultraviolet rays to convert one part of the surface into a hydrophilic surface. This conversion is performed based on digital data corresponding to an image to be printed. In this case, the hydrophobic portion is used as a printing image portion and the hydrophilic portion is used as a non-printing image portion. After completion of the printing, the compound is applied again to change the surface of the coat layer into the initial state of the printing plate as prepared, in which the surface of the coat layer exhibits hydrophobicity again.

[Elected Drawing] Figure 5

Fig. 1

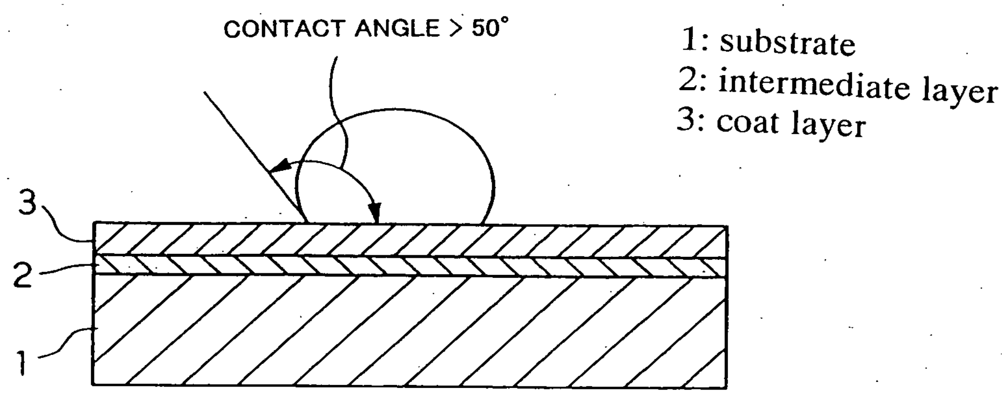

CONTACT ANGLE > 50°
1: substrate
2: intermediate layer
3: coat layer
3
2
1

Fig. 2

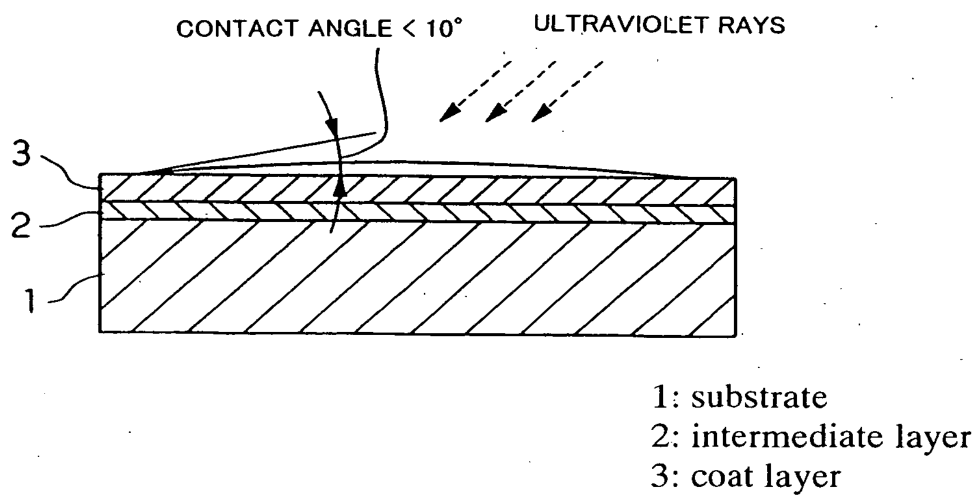

CONTACT ANGLE < 10°
ULTRAVIOLET RAYS
3
2
1
1: substrate
2: intermediate layer
3: coat layer

Fig. 3

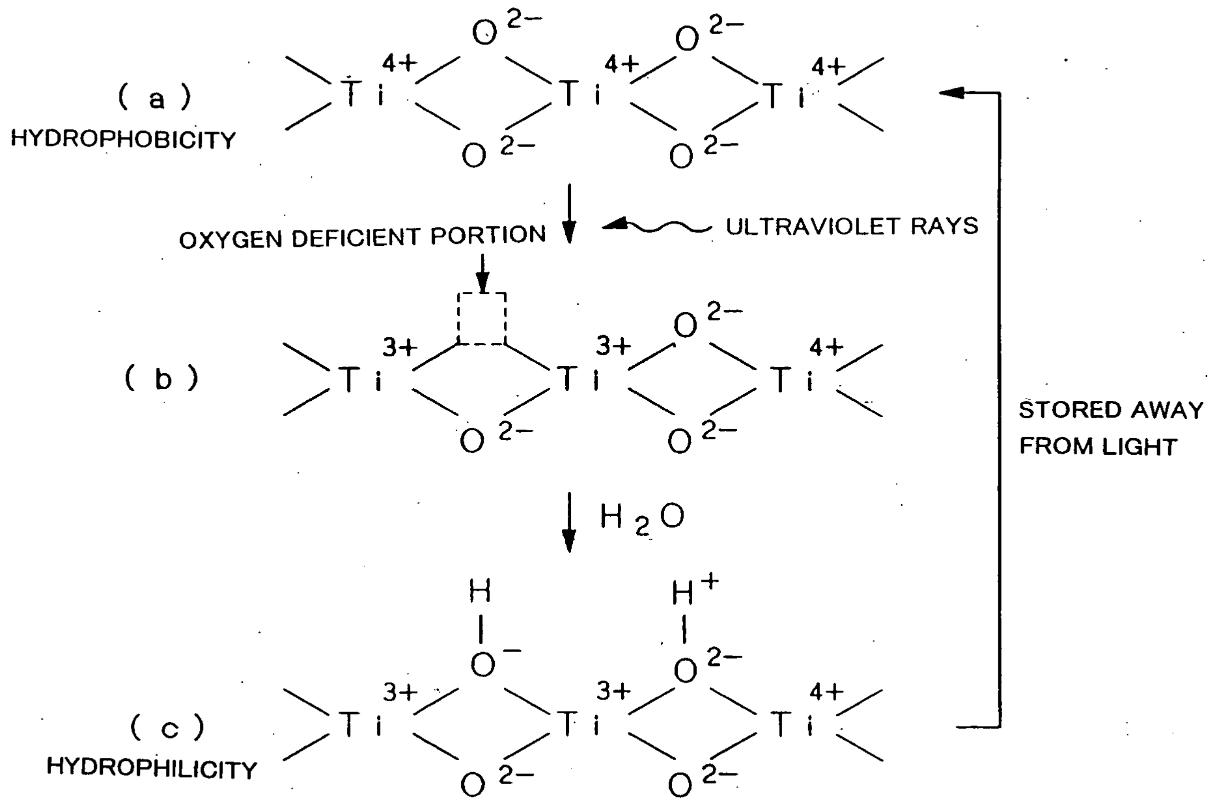
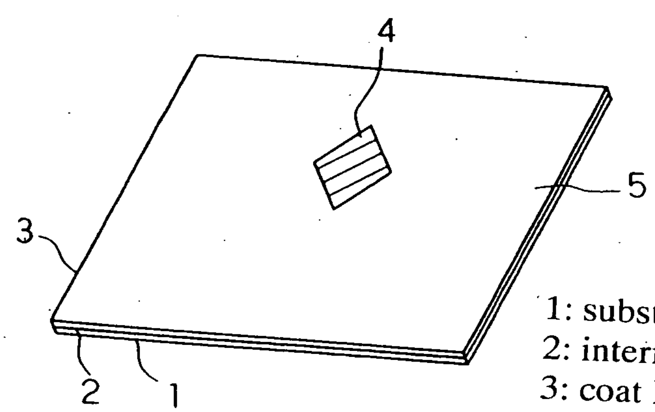


Fig. 4



1: substrate
2: intermediate layer
3: coat layer
4: image part
5: non-image part

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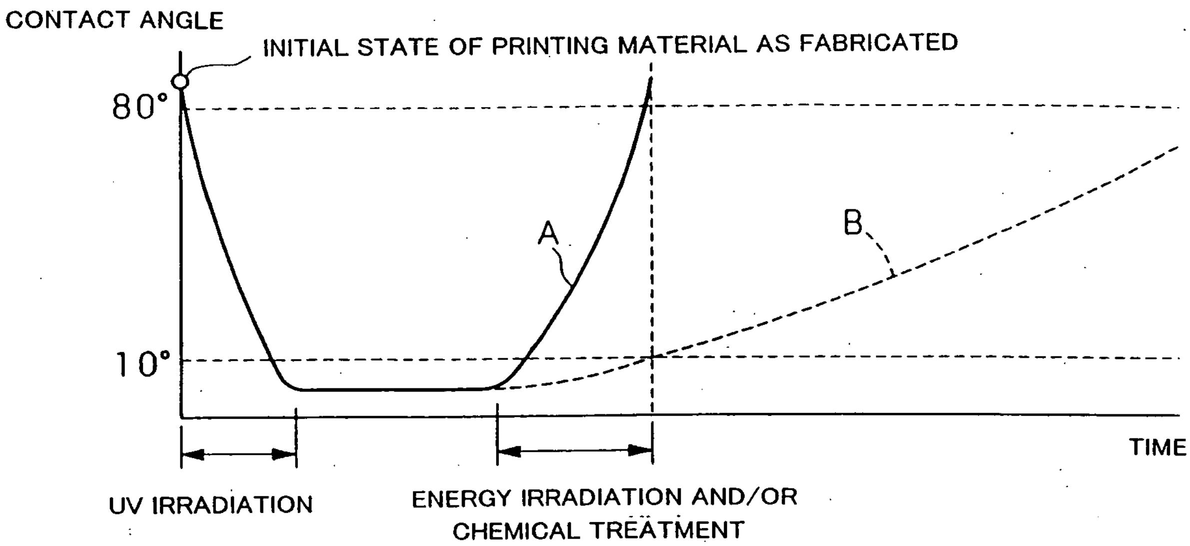
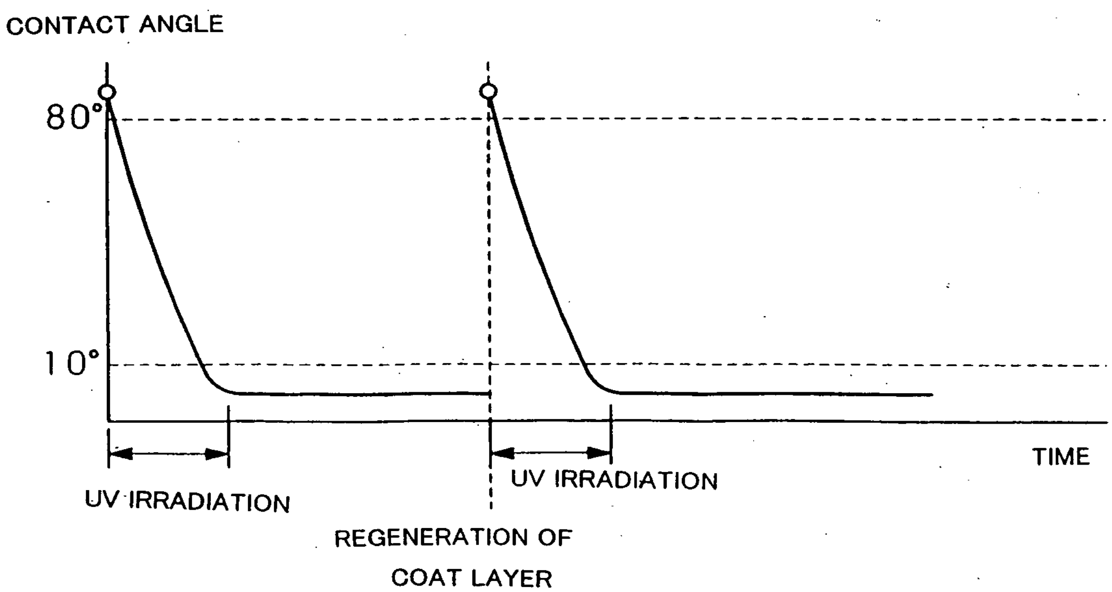
Fig. 5



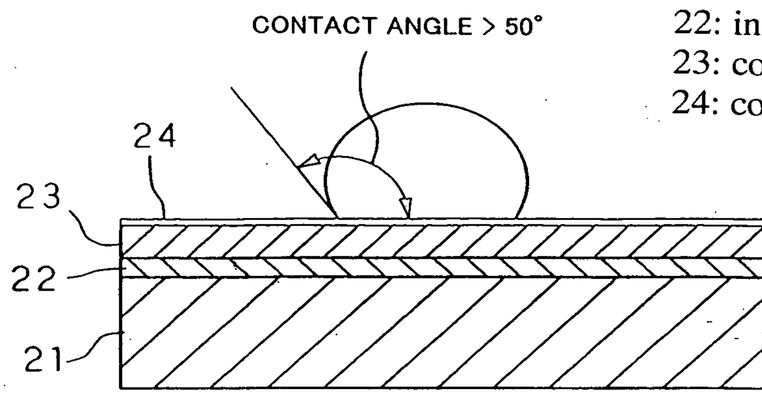
CONTACT ANGLE
INITIAL STATE OF PRINTING MATERIAL AS FABRICATED
80°
10°
A
B
TIME
UV IRRADIATION
ENERGY IRRADIATION AND/OR CHEMICAL TREATMENT

Fig. 6



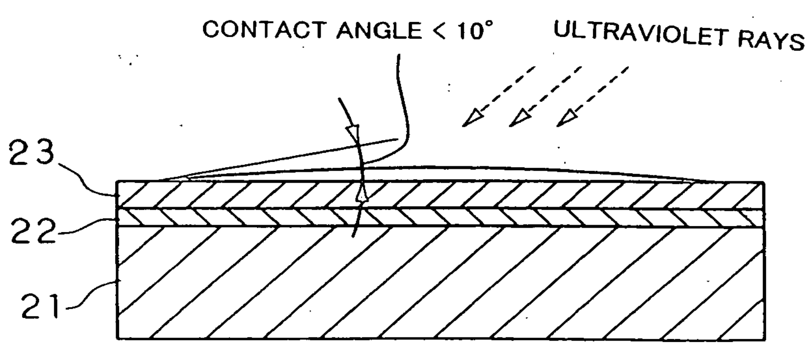
CONTACT ANGLE
80°
10°
TIME
UV IRRADIATION
UV IRRADIATION
REGENERATION OF COAT LAYER

Fig. 7



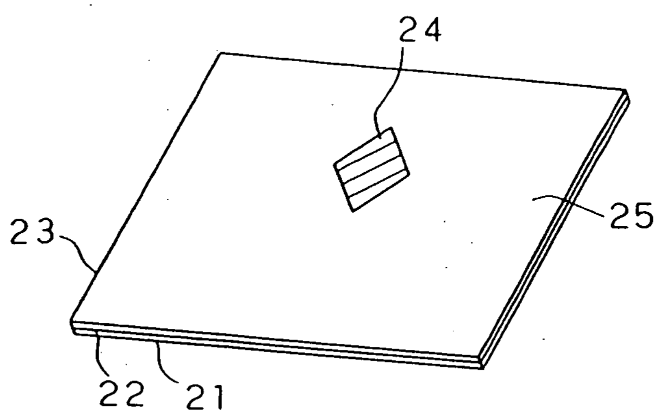
21: substrate
22: intermediate layer
23: coat layer
24: coating layer

Fig. 8



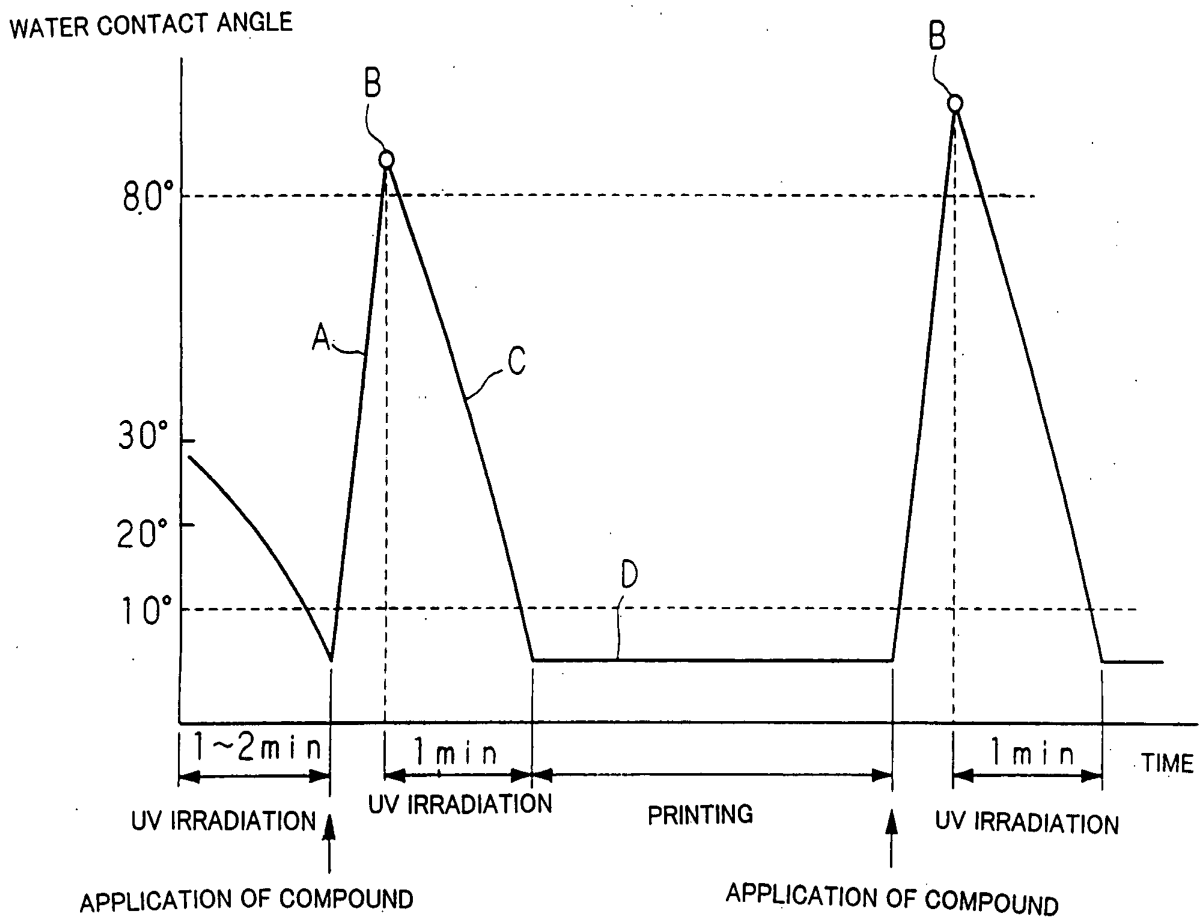
21: substrate
22: intermediate layer
23: coat layer

Fig. 9



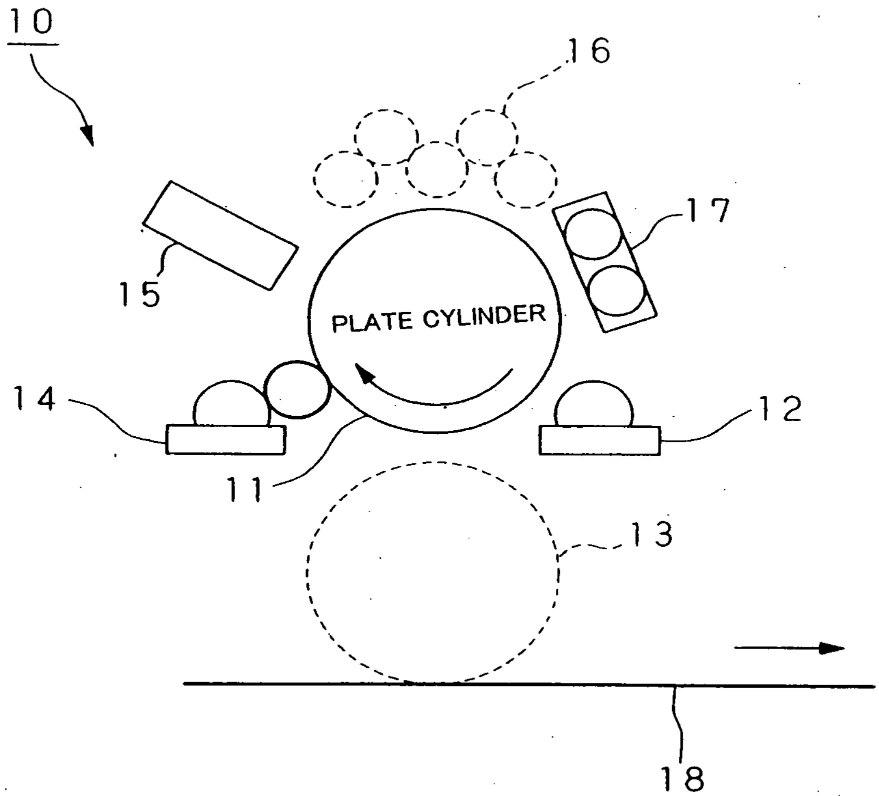
21: substrate
22: intermediate layer
23: coat layer
24: coating layer (image part)
25: non-image part

Fig. 10



WATER CONTACT ANGLE
80°
30°
20°
10°
B
A
C
D
B
1~2min
1min
1min
TIME
UV IRRADIATION
UV IRRADIATION
PRINTING
UV IRRADIATION
APPLICATION OF COMPOUND
APPLICATION OF COMPOUND

Fig. 11



10: printing machine
11: plate cylinder
12: coating apparatus
13: blanket cylinder
14: plate cleaning apparatus
15: writing apparatus
16: inking roller
17: drying apparatus
18: paper